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Nuclear quantum effects on the high pressure melting of dense lithium

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Using a self-developed combination of the thermodynamic integration and the *ab initio* path-integral molecular dynamics methods, we quantitatively studied the influence of nuclear quantum effects (NQE) on the melting of dense lithium at 45 GPa. We find that although the NQEs significantly change the free-energies of the competing solid and liquid phases, the melting temperature (T_m) is lowered by only ~ 15 K, with values obtained using both classical and quantum nuclei in close proximity to a new experiment. Besides this, a substantial narrowing of the solid/liquid free-energy differences close to T_m was observed, in alignment with a tendency that glassy states might form upon rapid cooling. This tendency was demonstrated by the dynamics of crystallization in the two-phase simulations, which helps to reconcile an important conflict between two recent experiments. This study presents a simple picture for the phase diagram of lithium under pressure. It also indicates that claims on the influence of NQEs on phase diagrams should be carefully made and the method adopted offers a robust solution for such quantitative analyses. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907752>]

I. INTRODUCTION

Lithium, being the lightest metallic element at ambient pressure, has long been considered as a “simple” metal. Recent advances in theory and experiment, however, have revealed a remarkably rich phase diagram with highly counterintuitive behaviors at high pressures and thus turned this field into a focus of intensive research.^{1–9} These behaviors include, for instance, phase transitions to solid structures with low symmetry,^{1,2} metal-insulator/insulator-metal transitions,^{3,4} the superconductivity at ~ 20 K,^{5,6} and the existence of a low-temperature liquid state at half million bar pressures.^{7,9,10} Taking the melting behavior of Li as an example, Li's high reactivity induces serious technical problems on handling it experimentally under pressure. The melting curve, consequently, remained unknown above 8 GPa until Lazicki and coworkers employed a multi-anvil cell technique to extend it to 15 GPa,¹¹ which helped them to find a maximum of the melting temperature (T_m) at ~ 10 GPa. Recently, Guillaume and coworkers remeasured this melting curve up to 60 GPa using diffraction techniques⁷ and reported a sharp drop of it above 15 GPa and an unexpected low T_m (~ 190 K) at ~ 40 GPa. This is the known lowest T_m among element crystals at this pressure range. By estimating the zero-point energy (ZPE), the authors suggested that the nuclear quantum effects (NQEs) play an important role in shaping this phase diagram.

Parallel to these experimental advances, *ab initio* molecular dynamics (MD) simulations also reported a decrease of T_m

above ~ 10 GPa.⁹ While the calculated T_m s through coexistence method agree well with existing experiments^{12,13} (including those appeared later in the experiments of Guillaume *et al.*) below ~ 30 GPa,⁷ the calculated T_m s between 40 and 60 GPa are higher than the experimental results in Ref. 7 by ~ 100 K. Considering the fact that the nuclei are treated as classical point-like particles in these simulations and the mass of lithium is relatively light, it was assumed that the NQEs could lower this melting temperature and rationalize this discrepancy. A more recent experiment by Schaeffer and coworkers, however, has revealed a completely different scenario,¹⁰ in which they have remeasured the T_m s by monitoring the electrical resistivity and visual appearance. Contrast to Guillaume *et al.*'s results at 40 to 60 GPa for the so-called Li-cI16 phase, their data adhere to the *ab initio* MD results in Ref. 9 over the whole pressure range till 60 GPa, i.e., $T_m \sim 300$ K, and consequently pose the question of how large the influence of the NQEs is on this T_m ?

As a matter of fact, this impact of the NQEs on the melting of element crystals has been a problem of general interest for many years. A prominent example is in the “holy-grail” system of high pressure physics, i.e., hydrogen,^{14,15} where a prediction of a low temperature metallic liquid state is well-known.^{16,17} Recently, it was demonstrated that this low temperature liquid state exists explicitly due to the NQEs.¹⁸ Lithium, as another most important example of the light-mass element crystal, has naturally become a target of such discussions. But to our surprise, we notice that except for the above mentioned suggestions concerning their possible influence on the phase diagram of Li,^{7,9,10} an explicit numerical study on this issue is sheer lacking. The main difficulty resides on the requirement that both the interatomic interactions and the statistical nuclear

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effects need to be accurately described, and these statistical effects include contributions from both thermal and quantum fluctuations. Besides, simulations of the melting also require some special treatment. One approach which is often used nowadays consists of considering simultaneously the solid and liquid within the same box.^{9,17,19} However, most studies along this direction are carried out using *ab initio* MD. The NQEs are absent. Only most recently, an attempt which combines *ab initio* path-integral molecular dynamics (PIMD) with this two-phase simulation method, where a quantum description of the nuclear statistical effects is allowed, has been reported on hydrogen.¹⁸ The second possible approach consists of calculating the free-energy of the solid and liquid phases separately as a function of temperature and pressure and then monitoring their competition. The most often used free-energy calculation method is thermodynamic integration (TI).^{20–23,27} Again, although it has been combined with the PIMD in some studies so that the NQEs on the free-energy are treated rigorously,^{24–27} *ab initio* descriptions of the interatomic potentials are still rare,²⁸ not even to mention applications to this problem.

In this manuscript, we quantitatively studied this problem by calculating the free-energies of the competing solid/liquid phases, using Li-cI16, the most well-defined solid state candidate structure at 45 GPa.^{7,9,10} Our simulations show that although the NQEs significantly change the free-energies of both the solid and liquid phases, T_m is lowered by only ~ 15 K, with both values obtained using both classical and quantum nuclei in close proximity to the experimental results of ~ 300 K in Ref. 10. Besides this and more interestingly, a substantial narrowing of the difference between the free-energies of the solid and liquid phases around T_m was observed, which is in alignment with a tendency that glassy state might form upon rapid cooling.^{7,10} By including the NQEs in the two-phase simulations, this tendency was partially confirmed by the dynamics of the crystallization process. These results present a simple, unified picture for the melting of dense lithium under pressure. In the meantime, the method adopted also gives a robust solution for rigorous analyses of the phase diagram of materials with light elements involved.

The paper is organized as follows. A description of the numerical details is given in Sec. II. In Sec. III, we analyze the results and identify the influence of NQEs on T_m and the dynamics of the crystallization process. Conclusions and perspectives are given in Sec. IV.

II. METHODS

Our simulations were performed using the Vienna *ab initio* Simulation Package (VASP), with a self-developed combination of the TI and the *ab initio* MD/PIMD methods.^{18,19,22} Perdew-Burke-Ernzerhof (PBE) functional within density-functional theory was used for descriptions of the electronic exchange-correlation interactions. Projector-augmented wave potentials (including 1s and 2s states as valence) were employed along with a 600 eV plane wave cutoff energy for the expansion of the Kohn-Sham orbitals. In the *ab initio* MD and PIMD simulations, we use the canonical (constant volume and constant temperature) ensemble. The Andersen thermostat was

used to control the temperature unless specified otherwise²⁹ in which the atomic velocities are periodically randomized by drawing them from a Maxwellian distribution every 80 fs (using a 2 fs timestep). This type of simulation generates the canonical ensemble and overcomes the ergodicity problem. A supercell containing 512 atoms was taken in the two-phase simulations, using Γ -point sampling, which gives a converged window of melting temperatures.^{19,30} In the calculation of the free-energies, a 216-atom supercell was chosen, using a k-mesh of $2 \times 2 \times 2$. Thermal electronic excitations are handled using the standard methods of finite-temperature DFT developed by Mermin.³¹ The electronic temperature is set to the physical temperature of the system. For the reported PIMD results, 12 beads were used to sample the imaginary-time path-integral, with 24 beads simulations performed to test their convergence. More general discussions about these numerical setups, convergence tests, and further computational details, please go to our supplementary material in Ref. 32.

The two-phase simulations were performed first using *ab initio* MD, which helped us to locate T_m within a range. Taking some temperatures within/beyond this range, we then calculate the free-energies of the competing liquid/solid phases with TI, using *ab initio* MD for the sampling of the configurational space. The free-energies of the harmonic lattice at the classical limit and the inverse power potential are taken as references, respectively, for the solid and liquid phases (see Ref. 32). This helped us to locate T_m at ~ 290 K. Then, we include contributions from the NQEs to these free-energies using a combination of the TI and *ab initio* PIMD methods. The λ -dependent effective potential for the polymer (with P beads) is defined as

$$V(x, \lambda) = \sum_{j=1}^P \left[\frac{1}{2} m \omega_n^2 (x_j - x_{j-1})^2 + \lambda V(x_j) + (1 - \lambda) V(x_c) \right], \quad (1)$$

where x stands for the spacial configuration of all the beads, x_j stands for the j th one, and x_c stands for their centroid. Upon taking $\lambda = 0$, the free-energy goes to the classical limit while taking $\lambda = 1$, one rigorously arrives at a quantum expression of this statistical quantity.³³ The difference between the free-energy of the system with classical and quantum nuclei is then evaluated by $\Delta F = \int_0^1 d\lambda F'(\lambda)$, where $F'(\lambda) = \langle \frac{1}{P} \sum_{j=1}^P [V(x_j) - V(x_c)] \rangle$.

III. RESULTS

We start our discussions with the coexistence simulations using classical nuclei. This is done by putting the solid and liquid phases in coexistence and running the *ab initio* MD simulations at different temperatures ranging from 220 to 330 K. Within a simulation time of 20 ps (using a 2 fs timestep), 270 K (300 K) was found to be the highest (lowest) temperature at which crystallization (liquefaction) occurs. This is reflected by the snapshots of the initial and final structures, as well as the mean square displacement (MSD) curves given in Fig. 1, where not only the ordered (disordered) final structures but also the zero (finite) slope of the MSD curve indicate that at 270 K (300 K) the system ends up with solid (liquid). In other

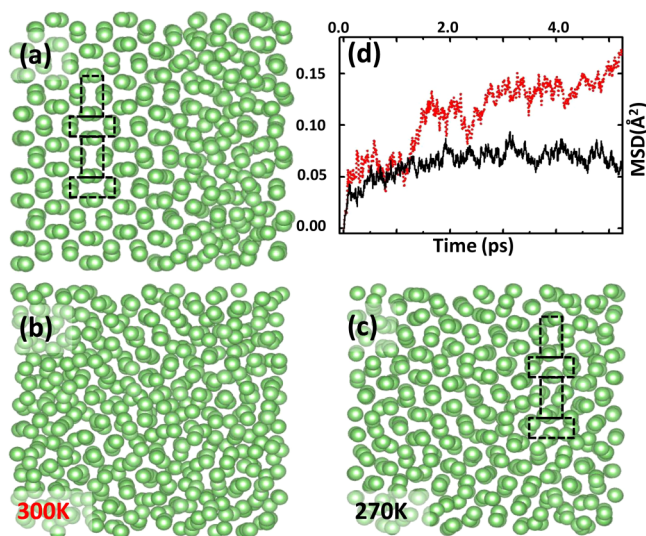


FIG. 1. Snapshots of the *ab initio* MD based two-phase simulations at 45 GPa showing (a) the starting structure, (b) and (c) the final states at 300 K and 270 K, respectively. The black dashed lines are used only to guide the eye for solid structure. (d) The MSD curves as a function of time for simulations at 300 K (red dotted line) and 270 K (black solid line) are also shown.

words, T_m lies within such a temperature range when the PBE functional is used for the description of the electron exchange-correlation interactions and a classical description of the nuclei is resorted to for its statistical effects, in good agreement with the results reported in Ref. 9.

Then, we choose four temperatures close to this range, i.e., 200, 250, 300, and 350 K, and calculate the free-energy of the competing solid (G^s) and liquid (G^l) phases using TI. The *ab initio* MD method was taken for the sampling of the configurational space. Therefore, only the classical thermal statistical effects are considered. By linearly fitting these data points at the four targeting temperatures, we show the evolution of the free energy difference with temperature in Fig. 2. T_m , the temperature at which $G^l - G^s$ equals zero, lies at ~ 290 K. This is in close proximity to the theoretical results in Ref. 9, where similar *ab initio* MD method was chosen to account for the nuclear statistical effects and the two-phase simulation method was used to get rid of the hysteresis effect.

Now, we add corrections from the NQEs to the free-energies using a combination of the TI and *ab initio* PIMD

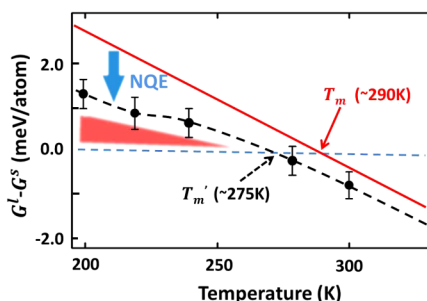


FIG. 2. Gibbs free energy differences between liquid and solid lithium as a function of temperature. When $G^l - G^s$ equals zero, the corresponding T means T_m . The red (black) line corresponds to results obtained with classical (quantum) nuclei using the combination of TI and *ab initio* MD (PIMD) methods.

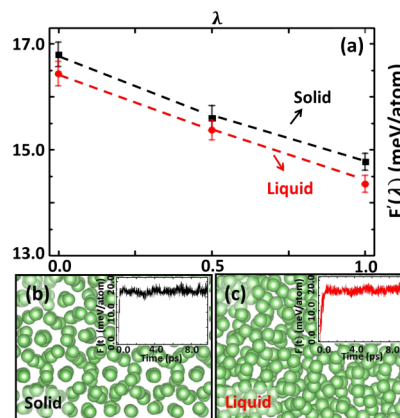


FIG. 3. (a) $F'(\lambda)$ as a function of λ for the solid (black square) and liquid (red sphere) lithium. The atomic structures of (b) solid and (c) liquid Li are shown together with $F'(t)$ as a function of time at λ equals 0, which is well-converged after 4.0 ps (see the insets).

methods (see Ref. 32 for details). An example for such simulations is shown in Fig. 3 when T equals 280 K. From this figure, it is clear that the NQEs have a strong influence on the free-energies of both the solid and the liquid phases (~ 15 meV/atom), with the value on the solid phase slightly larger. These influences, however, largely cancel each other and result in a reduction of $G^l - G^s$ by ~ 0.46 meV/atom at 280 K (see Fig. 2). For other temperatures, we perform similar calculations, add these corrections to the classical $G^l - G^s$, and show the results using a black dashed line in Fig. 2. A general trend is that this free-energy difference shifts down upon including the NQEs, and the magnitude for the corrections of the NQEs increases with decreasing T . T_m , the temperature at which $G^l - G^s$ equals zero, consequently decreases, with a magnitude of ~ 15 K. We notice that this decrease is much smaller than the discrepancy between the theoretical results in Ref. 9 (~ 300 K) and the experimental results in Ref. 7 (190 K). The values we obtained using both classical and the quantum nuclei are in close proximity to the more recent experimental results (~ 300 K) in Ref. 10. Therefore, although the NQEs have a large impact on the free-energy of the competing solid and liquid phases, its influence on T_m is much smaller than expected in the previous literatures. They are not the source of discrepancy between the theoretical results (in our study and in Ref. 9) and the experimental results in Ref. 7.

In the recent experiment, when the T_m of 300 K was reported (Ref. 10), it was claimed that the T_m of 190 K (Ref. 7) was an underestimation, and the formation of a super-cooled glassy state might be the reason. Interestingly, from our calculations of $G^l - G^s$ in Fig. 2, we see a substantial narrowing of this free-energy difference close to the melting point upon including the NQEs, especially below T_m . This narrowing means a decrease of the driving force for crystallization at the super-cooled region and, consequently, indicates that the NQEs favor formations of glassy states when rapid cooling occurs. We note that due to limitations of the simulation time (tens of ps), we can afford in comparison to the timescale in experiments (hours), it is unlikely to make a quantitative analysis on the formation of the glassy phase to complement

such experimental discrepancies. However, specifically concerning the NQEs, it is still possible to carry out an explicit investigation on their influence on crystallization close to T_m , by monitoring the dynamics.

Motivated by this, we take three temperatures below T_m (namely, 220, 240, and 260 K) and performed separate coexistence simulations using both classical and quantum nuclei. For all the two-phase simulations with classical nuclei, i.e., the *ab initio* MD based ones, the system crystallizes easily within 3 ps. While in all PIMD based simulations, the system does not reach an ordered state till the longest simulation time we can afford (20 ps). As PIMD simulations provide rigorously only thermally averaged NQEs when equilibrium is reached, we take T equals 240 K and perform a separate two-phase simulation using the partially adiabatic centroid MD (PACMD) approach within the path-integral scheme.^{34,35} A 0.05 fs timestep is used together with a Nosé-Hoover chain thermostat. This allows partial NQEs to be included in the dynamics. Again, a glassy state is reached in the end, as reflected by the MSD curve in Fig. 4. In comparison to this, the same MSD curve from the two-phase simulation based on *ab initio* MD shows an obvious process when large rearrangement of the atoms in favor of crystallization happens, before the

system reaches an ordered state. In other words, the NQEs clearly procrastinate crystallization. Whether this influence is significant enough to induce a glassy state at the experimental timescale is beyond the scope of this study. However, the substantial narrowing of the free-energy difference between the liquid and the solid phases and this obvious procrastination in its crystallization dynamics upon including the NQEs are in alignment with the likelihood that glassy state might form.

IV. CONCLUSIONS

The results reported here present a quantitative analysis for the influence of NQEs on the free-energies of the solid and liquid Li phases under pressure, which helps to clarify a fundamental problem in the melting behavior of Li. Our calculations show that although the NQEs significantly change the free-energy of both phases, these changes largely cancel and result in a shift of only ~ 15 K for the T_m toward lower temperatures at 45 GPa. The T_m s obtained using both classical and quantum nuclei (290 K and 275 K, respectively) are in close proximity to the experimental results in Ref. 10. Besides this, analysis of the dynamics in the two-phase simulations also shows that the NQEs procrastinate crystallization. These results combined together, present a unified theoretical picture for the melting of Li in the pressure range between 40 and 60 GPa, which is consistent with a recent experimental effort. More generally, concerning the high pressure phase diagrams of simple element crystals, claims on the influence of NQEs should be carefully made since the ZPEs on competing phases can cancel. Explicit calculations of this quantity on each phase, with anharmonic statistical effects originating from both thermal and quantum behaviors of the nuclei included, are highly recommended. The method used in the present study gives a robust recipe for studies on this direction.

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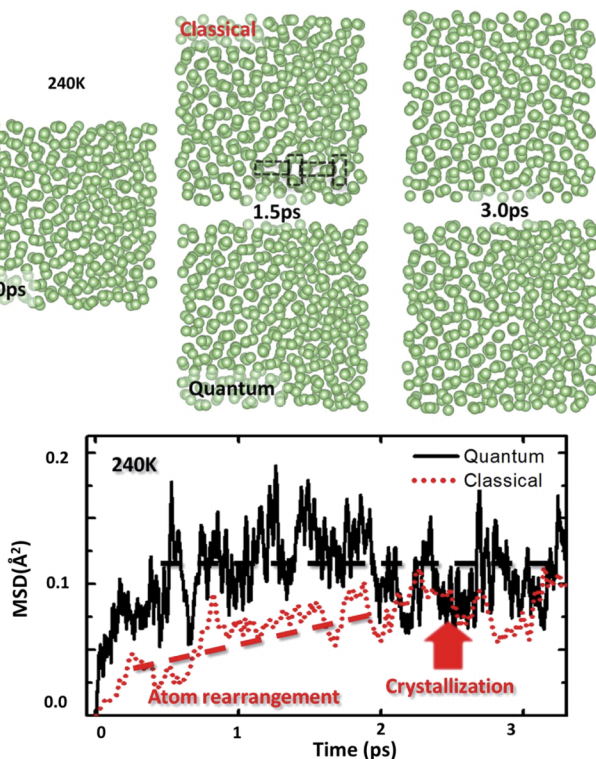


FIG. 4. At 240 K, the two-phase simulations using classical and quantum nuclei were compared. With classical nuclei, the system solidifies easily within 3 ps. While using quantum nuclei, glassy structures remain after 20 ps. Using partially adiabatic centroid MD (a modification of PIMD in which the dynamics can be analyzed), we compare the crystallization processes in the MD and PIMD simulations. In the simulations with classical nuclei, crystallization happens more easily, with a state for large rearrangement of the atoms and then crystallization. While in the simulations with quantum nuclei, the system reaches a disordered state quickly and gets trapped there. This is consistent with the analysis of the energetics as shown in Fig. 2, where a narrowing of the free-energy difference between the solid and liquid phase is observed.

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